
Supplementary information

Terahertz field-induced metastable magnetization near criticality in FePS₃

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Supplementary Information for "Terahertz field-induced metastable magnetization near criticality in FePS₃"

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1 Excitation pathways of 3.27 THz phonon

In Fig. 4a, we show the dependence of the 3.27 THz phonon amplitude on THz electric field. The fit function we used has both linear and quadratic terms ($|aE_{\text{THz}} + bE_{\text{THz}}^2|$), whereas these terms individually cannot fit the field dependence. Since both magnetic and lattice structures of FePS₃ preserve inversion symmetry [1], phonons are either Raman-active or infrared-active, but not both. The origins of linear and nonlinear excitation mechanisms are as follows. The 3.27 THz mode is Raman active, and hence can be excited nonlinearly with THz via two photon absorption or other nonlinear pathways, which more generally can be classified as sum- or difference-frequency generation of photonic or ionic modes [2]. As the Q_2 mode is also hybridized with a magnon even at zero external magnetic field [3], it can be linearly excited through magnon. The fact that the field dependence is curved down tells us about the destructive interference between these two driving forces on Q_2 mode.

2 Fluence dependence of other low energy phonons

In addition to the main modes of interest (magnon and 3.27 THz phonon) we detect three additional phonons, with symmetries that are not expected to induce a net magnetization as discussed in Section 5 below. The fluence dependence of the modes with frequencies higher than that of the magnon (4.80 THz and 7.51 THz), show a clear nonlinear behavior. Phonons that are lower than magnon in energy (2.64 THz and 3.27 THz) show a dependence close to linear (Extended Data Fig. 3), however there may be a nonlinear component as well, as expected from their Raman-active nature.

3 Dissipation of heat deposited by THz pulse

To understand the long-lived thermal response in the $\Delta\theta$ channel (Fig. 2a), we provide a semi-quantitative analysis of the heat dissipation time in FePS₃ $\tau_{\text{dis}}(T)$, defined as a characteristic time required for the system to cool back to initial temperature T_0 , after being heated up by a laser pulse to some temperature $T > T_0$. During this process, incident THz pulse heat up the sample portion within the spot size of the terahertz pulse ~ 1 mm, whereas the rest of the crystal stays at T_0 and serve as a bath to absorb the thermal energy. The thermal power dissipated from the heated region to the rest of the sample is proportional to their temperature differences as:

$$P_{\text{th}} \propto \kappa(T - T_0), \quad (1)$$

where κ is the thermal conductivity for the given contact area between the two regions. This transferred heat cools the heated region, as described by:

$$\kappa(T - T_0)\delta t = -C_s(T)\delta T, \quad (2)$$

where $C_s(T)$ is heat capacity of the spin subsystem. The characteristic time is therefore obtained by:

$$\int_0^{\tau_{\text{dis}}} \delta t = -\frac{1}{\kappa} \int_T^{T_0} \frac{C_s(T)}{T - T_0} \delta T \quad (3)$$

$$\Rightarrow \tau_{\text{dis}}(T_0) = -\frac{1}{\kappa} \int_T^{T_0} \frac{C_s(T)}{T - T_0} \delta T. \quad (4)$$

Here we assume that κ stays constant over temperature. The experimental temperature dependence of κ exhibits a small kink near T_N [4], which should not considerably affect the overall behavior of $\tau_{\text{dis}}(T)$. On the other hand, the heat capacity of the spin subsystem undergoes a sharp critical divergence at the transition temperature [5]. Therefore the characteristic heat dissipation time is also expected to exhibit a critical slowing down near the Néel temperature. The determination of the order of magnitude of τ_{dis} requires material specific values of the quantities involved.

4 Spin structure factor and magnetic susceptibility

The dynamical spin structure factor, which is a measure of magnetic correlations at a given frequency and wavevector $(\omega, \mathbf{k})$, is defined as

$$S_{\mathbf{q}}(\omega) = \frac{1}{N} \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \int dt e^{i\omega t} \langle \mathbf{S}_i(t) \cdot \mathbf{S}_j \rangle. \quad (5)$$

Here, we are mainly interested in the static spin structure factor obtained by taking the limit $\omega \rightarrow 0$, and given by

$$S_{\mathbf{q}} = \frac{1}{N} \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle. \quad (6)$$

Similarly the dynamical magnetic susceptibility is defined as

$$\chi_{\mathbf{q}}(\omega) = \frac{1}{N} \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \int dt e^{i\omega t} \left[\langle \mathbf{S}_i(t) \cdot \mathbf{S}_j \rangle - \langle \mathbf{S}_i(t) \rangle \cdot \langle \mathbf{S}_j \rangle \right], \quad (7)$$

and measures the response of a magnetic system to an external magnetic field $\mathbf{B}_{\mathbf{q}}(\omega)$. In the static limit it becomes

$$\chi_{\mathbf{q}} = \frac{1}{N} \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \left[\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle - \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle \right]. \quad (8)$$

Since near a second order phase transition the order parameter is finite across the transition temperature, the second term in the parentheses above will be regular. However, as the magnetic susceptibility is known to diverge for T approaching T_N [6], the first term in parentheses (physically the spin fluctuations) must diverge. Since the first term is nothing but the spin structure factor, we expect $S_{\mathbf{q}}$ to diverge as $\chi_{\mathbf{q}}$ at the critical temperature as

$$S \sim \chi \sim |T - T_N|^\gamma. \quad (9)$$

5 Microscopic Hamiltonian and effective spin-phonon coupling

5.1 Low-energy microscopic Hamiltonian

The low-energy magneto-elastic properties of FePS₃ can be described by a Hamiltonian of the form [3, 7]:

$$H = \sum_{ij} \mathbf{S}_i \cdot (\mathbf{J}_{ij} \mathbf{S}_j) - \Delta \sum_i (S_i^z)^2 + \frac{1}{2} \sum_{\alpha} \left[P_{\alpha}^2 + \Omega_{\alpha}^2 Q_{\alpha}^2 \right], \quad (10)$$

where the matrix $\mathbf{J}_{ij}$ encodes the (possibly anisotropic) couplings of spins $\mathbf{S}_i$ and $\mathbf{S}_j$, and Δ is a single ion anisotropy. Further, P_α and Q_α are the momentum and displacement operators of phonon mode α , respectively, and Ω_α is the corresponding phonon frequency. In general, the magnetic interactions depend on the atomic positions, giving rise to an interaction between the spins and the lattice displacements. For small displacements Q_α the exchange tensor can be expanded as

$$\mathbf{J}_{ij}(Q) \approx \mathbf{J}_{ij} - \alpha_{ij}Q, \quad (11)$$

where the tensor α_{ij} quantifies the phonon modulation of the magnetic interactions.

The magnetic exchange interactions as well as the modulations α_{ij} were calculated from first principles within the frozen phonon approximation (see Table S1 and Extended Data Table 2 for the calculated values and the Methods section for a discussion of the computational details). We identify four relevant phonon modes at $\Omega_1^{(c)} = 2.67$ THz, $\Omega_2^{(c)} = 3.27$ THz, $\Omega_3^{(c)} = 4.77$ THz and $\Omega_4^{(c)} = 7.48$ THz (see Extended Data Table 1), in good agreement with the frequencies observed in Raman [8] and infrared [3] spectroscopies. We find that α_{ij} decays rapidly with inter-atomic distance, and is significant only for nearest neighbor exchange interactions. Due to the space group symmetries of the system, only four nearest neighbor bonds of the magnetic unit cell are independent, and are henceforth labeled J_1 , J_2 , J_3 and J_4 in accordance with Fig. S1.

J_1^F	J_1^A	J_2^F	J_2^A	J_3	Δ
-0.56	-1.40	0.01	0.43	0.53	2.46

Table S 1. Equilibrium magnetic interactions parameters of FePS₃. The magnetic exchange interactions for nearest neighbor (subscript 1), next nearest neighbor (subscript 2) and third nearest neighbor interactions (subscript 3) used to obtain the equilibrium properties of FePS₃ via simulated annealing. The superscript denotes the interactions on intra-chain (ferromagnetic, F) and inter-chain (antiferromagnetic, A) bonds. The single-ion anisotropy is denoted by Δ .

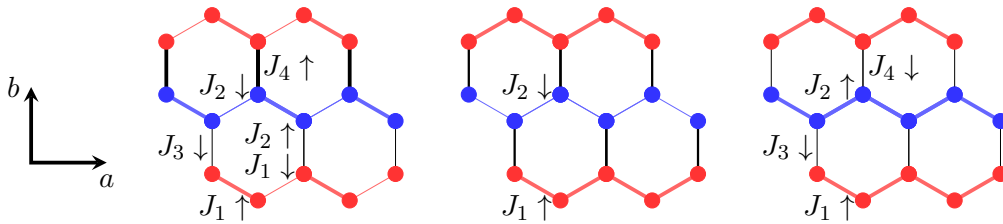


Fig. S 1. Spatial patterns of the phonon-modulated spin parameters. Modulation patterns of the magnetic parameters induced by phonon modes 1, 2 and 3 (the modulation pattern for mode 4 is equivalent to mode 1). An increase in the magnetic interaction on a given bond is illustrated by a thick line and an upward-pointing arrow $\uparrow$, while a decrease is illustrated by a thin line and a downward-pointing arrow $\downarrow$. Note that for modes 1 and 4 there is an additional modulation of the magnetic parameters J_1 and J_2 along the intra-chain (a -axis) direction.

5.2 Coarse-graining the spin-phonon coupling

The spatial patterns in which the phonons modulate the magnetic interaction parameters are shown in Fig. S1, while the strength of the couplings is reported in Extended Data Table 2. The diagonal components of α is much larger than the off-diagonal components therefore α can be treated as a scalar. Defining the zigzag (ZZ) antiferromagnetic and ferromagnetic (FM) order parameters $L = S_1 - S_2 - S_3 + S_4$ and $M = S_1 + S_2 + S_3 + S_4$, the microscopic modulations of the magnetic parameters can be mapped onto a theory of macroscopic variables. These macroscopic variables are expected to govern the low-energy and long wavelength behavior of the theory.

More specifically, we can write the spin-phonon couplings for phonon modes 2 and 3 as

$$\begin{aligned} H_{\text{int}}^{(2)} &= \gamma Q_2 (S_2 S_3 - S_1 S_4) \\ &= -\gamma Q_2 L M \end{aligned} \quad (12)$$

$$\begin{aligned} H_{\text{int}}^{(3)} &= \delta Q_3 (S_2 S_3 + S_1 S_4) - \epsilon Q_3 (S_1 S_2 + S_3 S_4) \\ &= \frac{Q_3}{2} (\delta - \epsilon) M^2 - \frac{Q_3}{2} (\delta + \epsilon) L^2, \end{aligned} \quad (13)$$

where Q_i is the phonon coordinate of mode i and γ , δ and ϵ are constants determining the strength of the coupling. For modes 1 and 4, which have equivalent spatial modulation patterns (see Fig. S1), the mapping to macroscopic variables also involves the columnar order parameter $C = S_1 + S_2 - S_3 - S_4$. Introducing this variable gives

$$\begin{aligned} H_{\text{int}}^{(1,4)} &= \gamma Q (-1)^x (S_2 S_3 - S_1 S_4) - \delta Q (S_1 S_2 - S_3 S_4) \\ &= \gamma Q - \delta Q C_1 M \end{aligned} \quad (14)$$

Since the columnar order parameter is zero for the magnetic exchange couplings of FePS₃, phonon modes 1 and 4 are not expected to play a significant role for the photo-induced magnetization dynamics. In the long wavelength (macroscopic) limit the dominant spin-phonon coupling is therefore expected to be of the form

$$H_{\text{int}} = -\gamma Q_2 L M + \frac{\delta}{2} Q_3 M^2 - \frac{\epsilon}{2} Q_3 L^2. \quad (15)$$

However, the coupling proportional to Q_3 is not found to generate a net magnetization either in microscopic Monte Carlo simulations or the effective Ginzburg-Landau theory discussed below, unless there is a mechanism breaking the degeneracy between opposite magnetizations. Therefore we neglect the effect of this phonon as well.

6 Spin Monte Carlo simulations with frozen phonons

To validate the connection between the microscopic spin-phonon Hamiltonian and the coarse-grained interaction discussed in the previous section, we performed simulated annealing for an FePS₃ monolayer using the Metropolis Monte Carlo algorithm (see Methods for the computational details). With the equilibrium spin parameters as given in Table S1 and a spin length $S = 2$, the simulations predict a magnetic phase transition from the paramagnetic to the zigzag antiferromagnetic state at a Néel temperature $T_N \approx 115$ K,

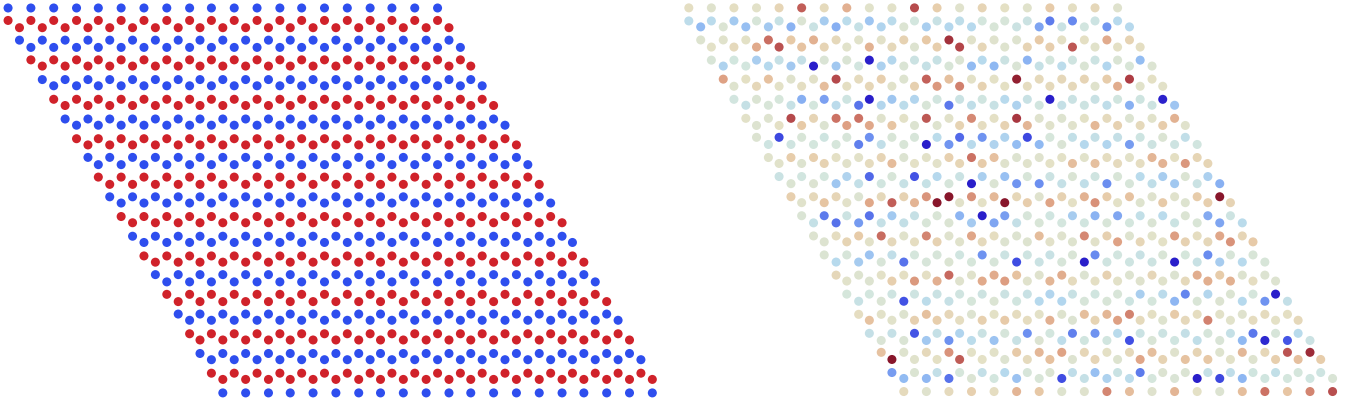


Fig. S 2. Equilibrium and light induced magnetic order of FePS₃. **a**, Equilibrium magnetic order of a 20×20 supercell of monolayer FePS₃, as obtained via spin Monte Carlo simulations. **b**, The difference $\mathbf{S}_i - \mathbf{S}_i/|\mathbf{S}_i|$ between the actual magnetic state and a perfect collinear (Ising) state, for a modulation of the magnetic parameters corresponding to the 3.27 THz phonon mode. A slight canting of the spins gives rise to a net magnetization around T_N .

resulting in the low-temperature magnetic state shown in Fig. S2. The transition temperature is in good agreement with the experimentally observed value, thereby validating our microscopic model.

To assess the effects of spin-phonon coupling, the magnetic parameters were modified to include a static modulation in accord with the spatial modulation patterns of Fig. S1. Such simulations are consistent with the frozen phonon approximation used to obtain the parameters, and reveal the expected magnetic properties for a fixed phonon displacement Q_i . For modes 1, 3 and 4 no qualitative effect is seen on the order parameters L and M , or on the transition temperature. In contrast, for a finite displacement of phonon mode 2 (i.e. for $Q_2 \neq 0$), a finite magnetization appears in connection with the magnetic phase transition (see Figs. S2 and S3), an effect which is independent of system size and thus expected to survive in the thermodynamic limit. This strongly indicates a significant coupling between the phonon coordinate $Q = Q_2$ and the macroscopic order parameters L and M .

To determine the form of the interaction, we note that the magnetization grows linearly with the phonon coordinate Q_2 (see Fig. S3). Further, we find that the sign of the magnetization is sensitive to the sign of both Q_2 and L , and determined by the sign of the product $Q_2 L$ (see Fig. S3). Due to Raman-activity and its intricate connection to the AFM ordering, the sign displacement of the Q_2 phonon depends on underlying order (L), rendering the sign of magnetization independent of the THz field polarization (see Supplementary Note 13 for a detailed discussion). The lowest order interaction term consistent with these results is of the form $\gamma Q_2 L M$, in agreement with the coarse-graining performed in the previous section. We note that here we did not introduce the effect of critical fluctuations and therefore cannot capture the behavior at $T > T_N$.

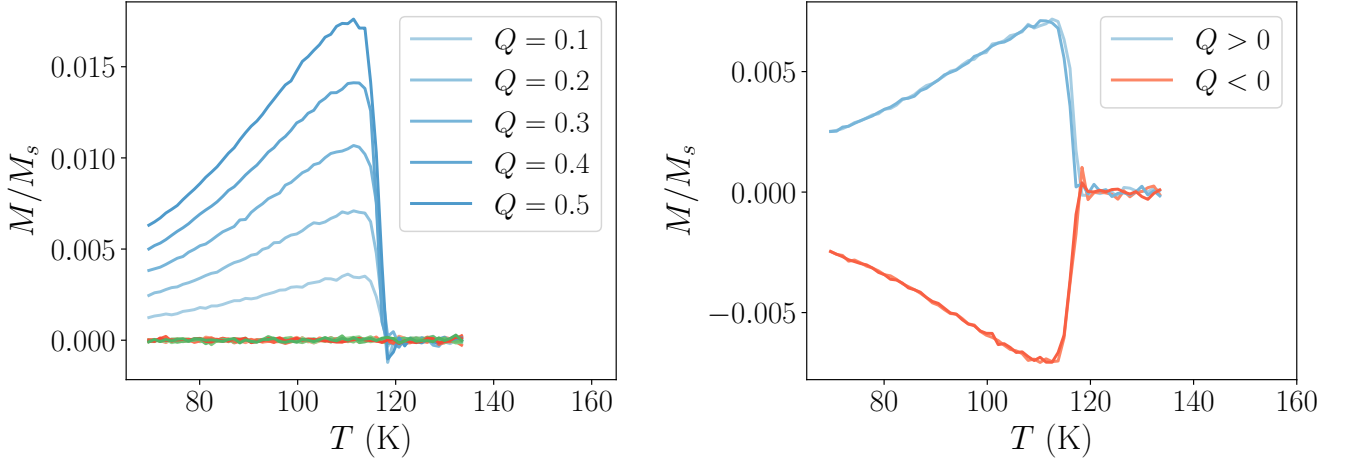


Fig. S 3. Temperature and phonon displacement dependence of induced magnetization in FePS₃. Temperature dependence of the phonon-induced magnetization of FePS₃, as a function of amplitude and sign of the phonon coordinate $Q = Q_2$. The phonon modulations are given in terms of the basic unit $Q_0 = 0.43$ pm. These results are consistent with a spin-phonon coupling of the form Q_2LM . We did not introduce the effect of critical fluctuations here and therefore cannot capture the behavior at $T > T_N$.

7 Effective Ginzburg-Landau theory

Based on the results of the previous sections, we formulate a Ginzburg-Landau theory in terms of the magnetic order parameters L and M as well as the phonon coordinate Q_2 . The most general symmetry-allowed form of the free energy is, up to fourth order in L and M

$$F = \frac{a_L(T)}{2}L^2 + \frac{b_L}{4}L^4 + \frac{a_M(T)}{2}M^2 + \frac{b_M}{4}M^4 + \frac{\Omega}{2}Q_2^2 + gLMQ_2. \quad (16)$$

The resulting free energy landscape for a given phonon displacement is shown in Fig. 4d of the main text. Here we could in principle also include terms of the form $g_{QM}Q_3M^2 + g_{QL}Q_3L^2$, consistent with the coarse-graining procedure. However, since our spin Monte Carlo simulations show no induced magnetization in response to a distortion along the Q_3 mode, we assume this coupling is negligible.

In the following we assume that the effects of the phonon on the dominant order parameter L are small, such that we can keep L constant while minimizing the free energy. This is supported by the results of Fig. S4, demonstrating the insensitivity of the zigzag order susceptibility to a finite magnetization. The equilibrium configuration of M and Q_2 can then be found by solving the equations

$$\begin{aligned} 0 &= \frac{\partial F}{\partial M} = a_M M + b_M M^3 + gLQ_2 \\ 0 &= \frac{\partial F}{\partial Q_2} = \Omega^2 Q + gLM. \end{aligned} \quad (17)$$

For a fixed Q_2 , and assuming $M \ll 1$ such that the b_M term is negligible, we find $M = -(g/a_M(T))Q_2L$. This expression is consistent with the Monte Carlo simulations of Fig. S3 at fixed Q_2 , and can in principle

be used to fit to the expression $a_M(T) = a_{M0}(T - T_c)^{\gamma_M}$. Alternatively, the Ginzburg-Landau equations can be solved to obtain the self-consistent equilibrium values of M and Q_2 . This gives $Q_2 = -(g/\Omega)LM$ and

$$M = \pm \sqrt{\frac{g^2 \langle L^2 \rangle / \Omega - a_M(T)}{b_M}}. \quad (18)$$

To understand the implications of this expression, we note that L^2 is related to the spin structure factor $S_{\mathbf{q}}$ by $\langle L^2 \rangle = S_{\mathbf{q}_{zz}}$, where $\mathbf{q}_{zz}$ is the zigzag antiferromagnetic ordering vector. The spin structure factor is in turn related to the magnetic susceptibility χ_{zz} of the zigzag order (see Supplementary Note 4 above), which is expected to diverge at the critical temperature like $\chi_{zz} = \chi_0 |T - T_N|^{-\gamma}$. Therefore, for temperatures close to T_N , we have (using $S = S_0 |T - T_N|^{-\gamma}$)

$$M = \pm g \sqrt{\frac{S_0}{b_M}} |T - T_N|^{-\gamma/2}. \quad (19)$$

In equilibrium the fluctuations in M between the solutions of opposite sign prevent the build-up of any net magnetization. However, when the system is driven into an asymmetric configuration by a finite phonon displacement Q_2 , a critical response is expected close to the phase transition.

We note that a fit to the temperature dependence of the observed rise time gives a critical exponent $\gamma/2 = 0.59 \pm 0.013$, which can be compared to the expected behavior for FePS₃. Due to its large easy-axis anisotropy, FePS₃ is to a very good approximation a 3-D Ising magnet, for which $\gamma/2 = 0.62$. Thus, the simple model considered here is in a good agreement with the experimental findings of Fig. 2 in the main text.

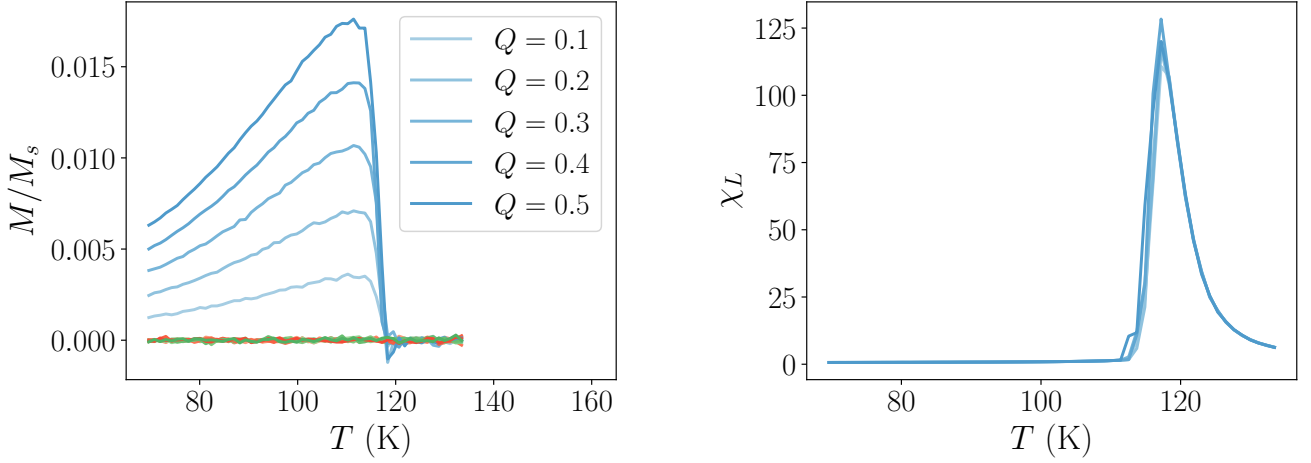


Fig. S 4. Effect of the magnetization on the critical properties of the antiferromagnetic order. A net magnetization and antiferromagnetic susceptibility as functions of temperature for different static phonon displacements. The susceptibility is seen to be insensitive to a finite phonon displacement and magnetization.

8 Mechanism of nonlinear phonon excitation

The physical picture emerging is that nonlinear driving of the 3.27 THz phonon mode breaks the degeneracy between the solutions to the Ginzburg-Landau equations, thereby inducing a finite magnetization. The return to an equilibrium magnetic configuration as $T \rightarrow T_N$ is then hindered by critical fluctuations with diverging lifetime, resulting in an exponentially long-lived nonequilibrium state.

To complete the picture, we here discuss the most likely excitation paths for the 3.27 THz phonon. Based on our 2-D THz spectroscopy results (Fig. S5), the 3.27 THz phonon is dominantly excited via an IR-active mode at 4.85 THz. The weak spectral weight along vertical axis indicates an additional photonic excitation mechanism of the 3.27 THz mode. For completeness, we include both the 4.2 THz and 4.85 THz modes for solving the equations of motion, and later will present the results only with 4.85 THz mode in Fig. S 8. Treating these modes as classical harmonic oscillators, and including the nonlinear coupling channels responsible for net phonon displacements, the phonon Hamiltonian is written as:

$$\begin{aligned}
 H_{\text{ph}} = & \frac{\Omega_2}{2}(P_2^2 + Q_2^2) + \frac{\Omega_{\text{IR},1}}{2}(P_{\text{IR},1}^2 + Q_{\text{IR},1}^2) + \frac{\Omega_{\text{IR},2}}{2}(P_{\text{IR},2}^2 + Q_{\text{IR},2}^2) \\
 & + \alpha_1(Q_2 Q_{\text{IR},1}^2 + Q_2^2 Q_{\text{IR},1}) + \alpha_2(Q_2 Q_{\text{IR},2}^2 + Q_2^2 Q_{\text{IR},2}) \\
 & + \beta_1 Q_2 Q_{\text{IR},1} E(t) + \beta_2 Q_2 Q_{\text{IR},2} E(t) \\
 & + z_{\text{IR},1} Q_{\text{IR},1} E(t) + z_{\text{IR},2} Q_{\text{IR},2} E(t) + R_2 Q_2 E^2(t).
 \end{aligned} \tag{20}$$

Here the variables $Q_{\text{IR},1}$ and $Q_{\text{IR},2}$ denote the coordinates of 4.2 THz and 4.8 THz IR phonons, respectively, while Q_2 denotes the coordinate of the Raman phonon at 3.27 THz. The terms proportional to α_i correspond to a non-linear phonon coupling giving a purely ionic excitation mechanism, whose geometry is illustrated in Fig. S6. Further, the terms proportional to β_i provide a channel for infrared-resonant Raman scattering, and the terms proportional to z_i and R_i give a direct coupling to the electric field via the Born

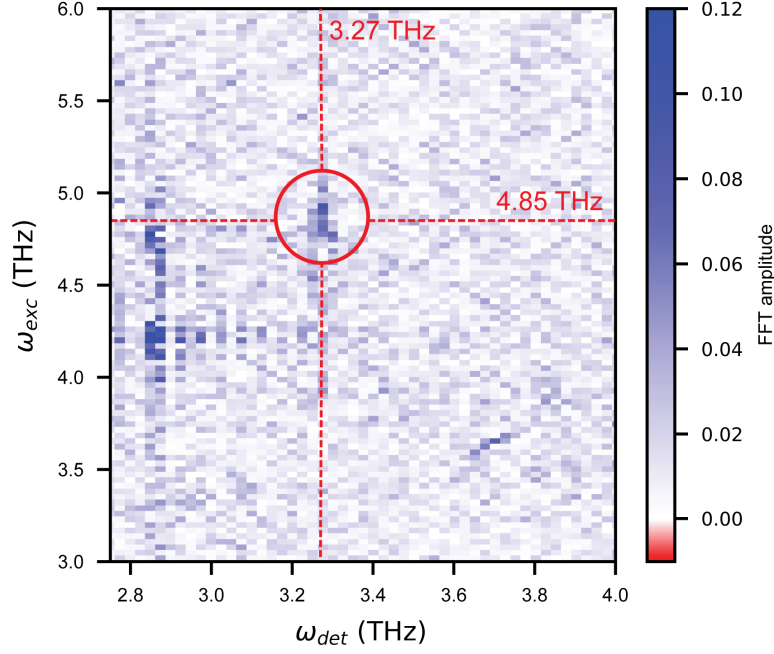


Fig. S 5. 2D THz spectrum of FePS₃. The cross peak (red circle) at the intersection of 3.27 THz Raman-active and 4.85 THz infrared-active phonon modes directly indicate their coupling. The weak spectral weight along vertical axis indicates an additional photonic excitation mechanism of the 3.27 THz mode.

effective charge tensor (for the IR phonons) or the Raman tensor (for the Raman phonon). Given this Hamiltonian, the phonon equations of motion are given by

$$\begin{aligned}
 \ddot{Q}_{IR,1} + \gamma_{IR,1}\dot{Q}_{IR,1} + \frac{\partial H_{ph}}{\partial Q_{IR,1}} &= 0 \\
 \ddot{Q}_{IR,2} + \gamma_{IR,2}\dot{Q}_{IR,2} + \frac{\partial H_{ph}}{\partial Q_{IR,2}} &= 0 \\
 \ddot{Q}_2 + \gamma_2\dot{Q}_2 + \frac{\partial H_{ph}}{\partial Q_2} &= 0
 \end{aligned} \tag{21}$$

The coefficients γ_i give a phenomenological description of the phonon damping.

As seen from Fig. S6, the initial excitation of the IR-active phonons via the THz field generates a net displacement of the lower Raman mode. Interestingly, when the lifetime of either of the IR phonons becomes long, also the Raman phonon becomes long lived. This feature can be understood by noting that the two upper modes keep transferring energy into the lower phonon. As illustrated in Fig.S 7 and Fig. S 8, the ionic excitation mechanism is found to be larger than the IRRS and photonic mechanisms by about an order of magnitude, indicating that it constitutes the main excitation mechanism.

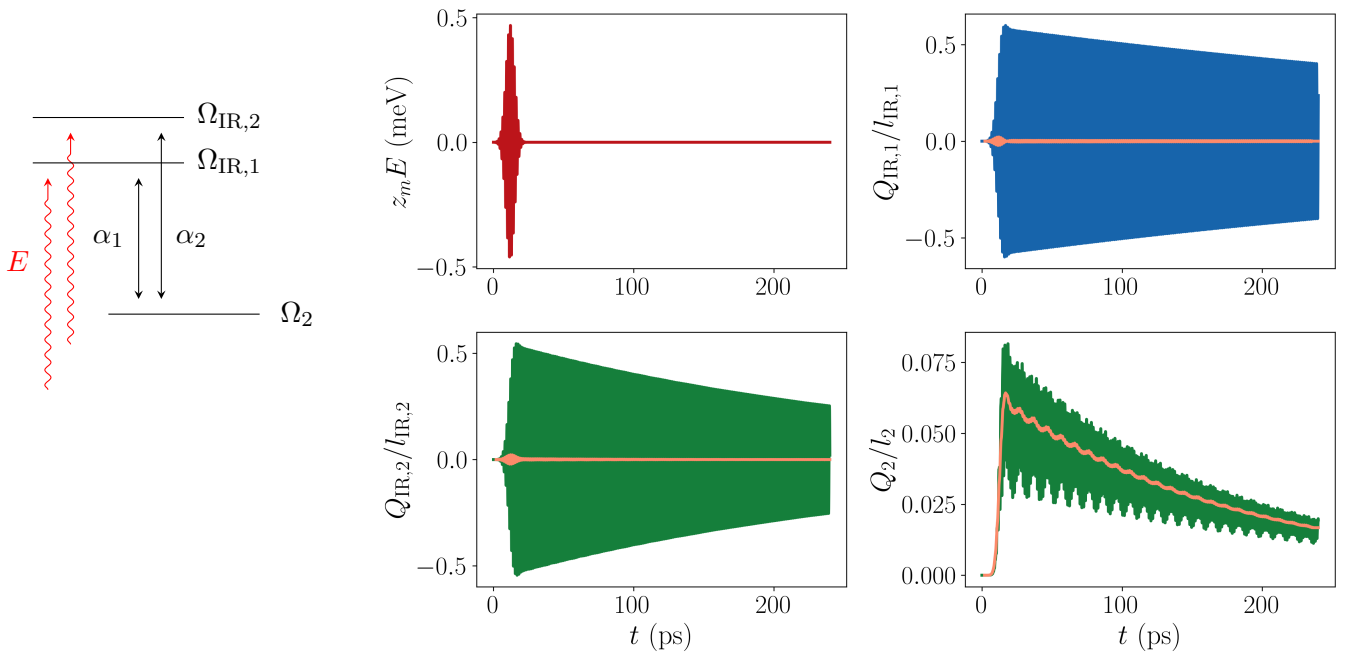


Fig. S 6. Coupled magnon-phonon dynamics induced by a THz field. Time dependence of the THz electric field E , the two IR phonon coordinates $Q_{\text{IR},1}$ and $Q_{\text{IR},2}$, as well as the Raman phonon coordinate Q_2 . The orange traces show period-averaged oscillation amplitudes illustrating the net displacements. All oscillator amplitudes are given in units of the oscillator length $l_i = \sqrt{\hbar/M_i\Omega_i}$.

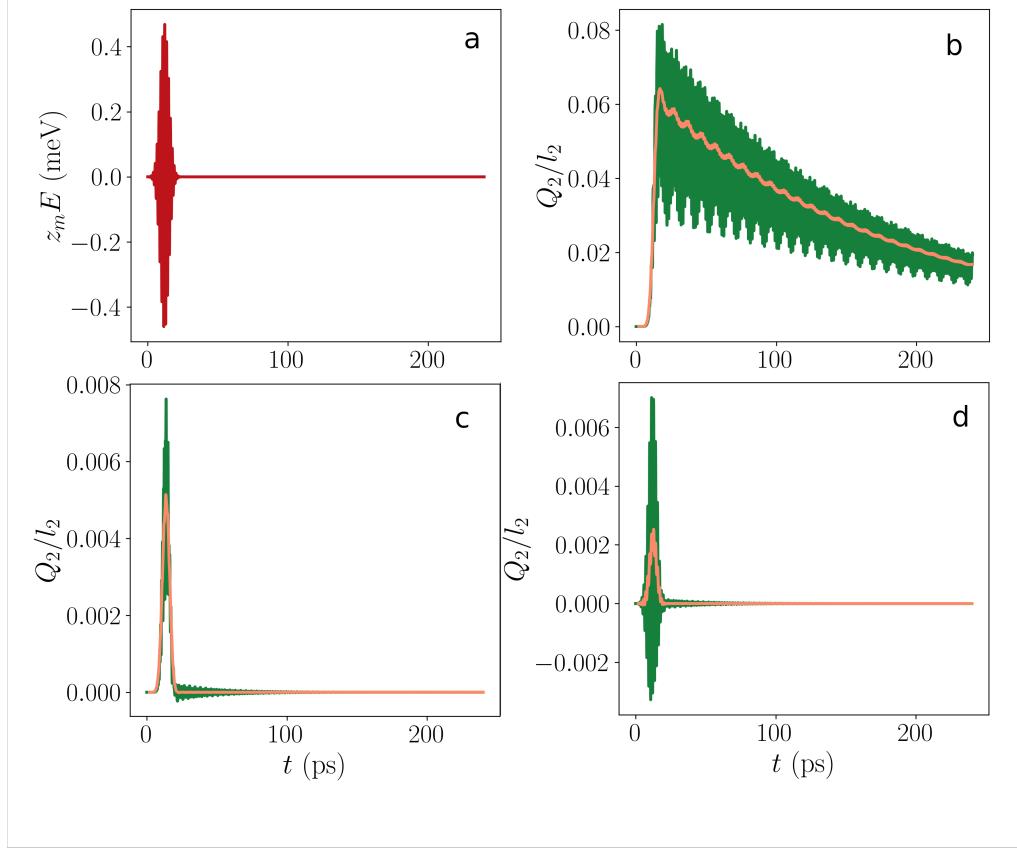


Fig. S 7. Comparison of different phonon excitation mechanisms. **a**, Time dependence of the THz electric field E . **b**, The Raman phonon coordinate Q_2 resulting from an ionic excitation mechanism. **c**, The Raman phonon coordinate Q_2 resulting from infrared-resonant Raman scattering. **d**, The Raman phonon coordinate Q_2 resulting from a purely photonic excitation mechanism. All oscillator amplitudes are given in units of the oscillator length $l_2 = \sqrt{\hbar/M_2\Omega_2}$, and the parameters are chosen such that $\alpha_i = \beta_i$ and $R_2 = \alpha_1 + \alpha_2$ in order not to bias the results.

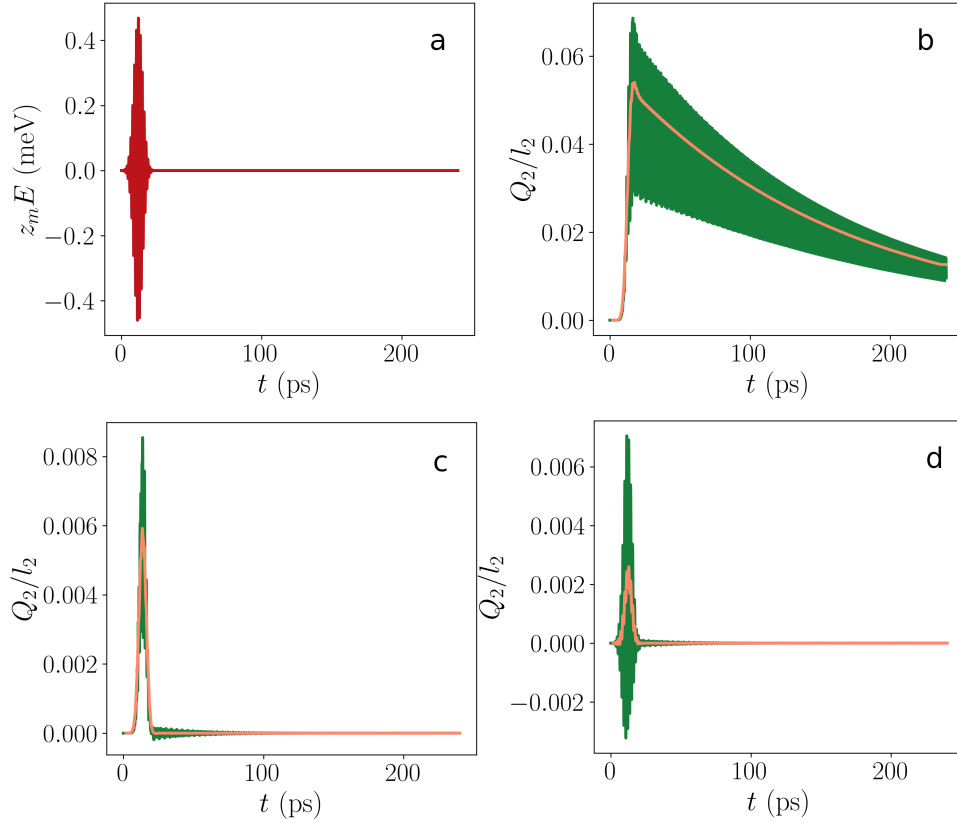


Fig. S 8. Comparison of different phonon excitation mechanisms involving the 4.8 THz phonon. **a**, Time dependence of the THz electric field E . **b**, The Raman phonon coordinate Q_2 resulting from an ionic excitation mechanism. **c**, The Raman phonon coordinate Q_2 resulting from infrared-resonant Raman scattering. **d**, The Raman phonon coordinate Q_2 resulting from a purely photonic excitation mechanism. All oscillator amplitudes are given in units of the oscillator length $l_2 = \sqrt{\hbar/M_2\Omega_2}$, and the parameters are chosen such that $\alpha_2 = \beta_2 = R_2$ in order not to bias the results. Only the 4.8 THz IR phonon is included here, which is modeled by taking $\alpha_1 = \beta_1 = 0$.

9 Initial short time dynamics

9.1 Ginzburg-Landau dynamics

From the free energy introduced above, we can also derive a set of coupled dynamical equations for the order parameters. In general, the equation of motion of a variable A appearing in the Ginzburg-Landau free energy is $\partial_t A = -\Gamma_A \partial_A F$ [9, 10], where Γ_A is a phenomenological damping rate. The phonon coordinate is assumed to satisfy the canonical equation of motion of a damped harmonic oscillator with the force term taken as $\partial_Q F$. The equations of motion thus become

$$\begin{aligned}\frac{\partial L}{\partial t} &= -\Gamma_L [a_L L + b_L L^3 + gMQ] \\ \frac{\partial M}{\partial t} &= -\Gamma_M [a_M M + b_M M^3 + gLQ] \\ \frac{\partial^2 Q}{\partial t^2} &= -[\Omega^2 Q + \Gamma_Q P + gLM],\end{aligned}\tag{22}$$

where P is the phonon momentum, and we have assumed that field-induced initial dynamics takes place on short time-scales compared to the intrinsic relaxation, such that any stochastic noise terms can be neglected.

As shown in Fig. S9, a kick of the phonon momentum induces a finite magnetization. In fact, within the classical Ginzburg-Landau framework the state with a finite $M = M_0$ and $Q_2 = Q_0$ is the true minimum of the free energy as long as L is finite. Therefore this state is expected to be long lived, and the system will return to its equilibrium state only through the relaxation of L . Such long-term dynamics can be qualitatively addressed by adding a stochastic term to the equations of motion, mimicking the thermal fluctuations [10]. The relaxation dynamics is discussed in detail in Supplementary Note 10.

9.2 Spin dynamics simulations

To supplement the Ginzburg-Landau dynamics, we performed real time simulations of the atomistic spin system. For this purpose we consider the spin-phonon Hamiltonian:

$$\begin{aligned}H &= \sum_{ij} \mathbf{S}_i \cdot (\mathbf{J}_{ij} \mathbf{S}_j) - \Delta \sum_i (S_i^z)^2 + \frac{1}{2} \sum_i [P_i^2 + \Omega_i^2 Q_i^2] + \gamma Q_2 \sum_{ij} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \\ &+ gQ_2 Q_{\text{IR}}^2 + ZE(t)Q_{\text{IR}},\end{aligned}$$

including two phonon modes at 3.27 THz and 4.8 THz (mode 2 and the upper IR-active mode) and the electric field $E(t)$ of the laser. For simplicity the 4.8 THz mode is considered to be linearly driven, but the exact driving scheme has little effect on the final result as long as it offers a channel for the 3.27 THz mode (mode 2) to be nonlinearly excited. The same conclusion can be reached by considering an excitation process proceeding via the magnon mode. The Hamiltonian leads to the following equations of motion:

$$\begin{aligned}\frac{\partial \mathbf{S}_i}{\partial t} &= \mathbf{S}_i \times \frac{\partial H}{\partial \mathbf{S}_i} \\ \frac{\partial^2 Q_2}{\partial t^2} &= -\Omega_2^2 Q_2 - gQ_{\text{IR}}^2 - \gamma \sum_{ij} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j\end{aligned}\tag{23}$$

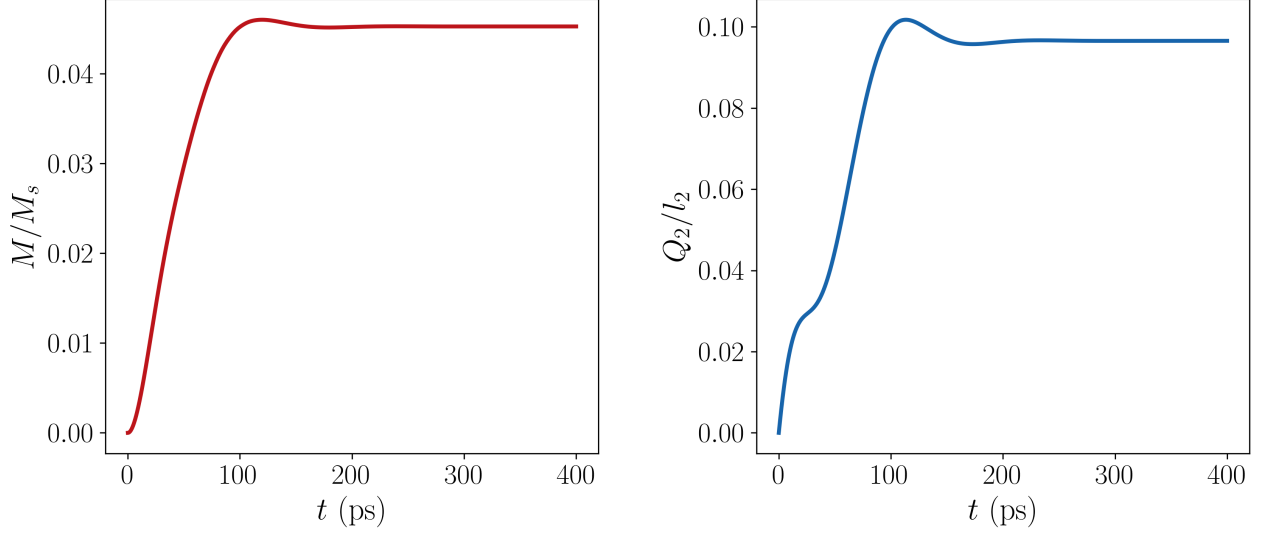


Fig. S 9. Ginzburg-Landau dynamics of net magnetization. Dynamics of net magnetization M and the phonon coordinate Q_2 following an initial kick of the phonon momentum to $P_0 = 0.1$. The magnetization is given in terms of the saturation magnetization M_s , and the phonon amplitude in terms of the oscillator length $l_2 = \sqrt{\hbar/M_2\Omega_2}$. The parameters are taken as $a_M = 0$, $b_M = 15$ THz, $\Omega = 3.27$ THz, $g = 1$ THz, $\Gamma_M = 13$ THz and $\Gamma_{Q_2} = 1.3$ THz.

$$\frac{\partial^2 Q_{\text{IR}}}{\partial t^2} = -\Omega_{\text{IR}}^2 Q_{\text{IR}} - 2gQ_2Q_{\text{IR}} + ZE(t).$$

We assume an electric field of the form

$$E(t) = \frac{E}{\sqrt{2\pi}\sigma} e^{-(t-\tau)^2/2\sigma^2} \cos(\Omega_{\text{IR}}t), \quad (24)$$

which induces oscillations in the upper phonon mode that in turn generate a rectified motion of the lower phonon mode via the nonlinear phonon coupling g . The lower phonon mode then induces a ferromagnetic magnetization in the spin system (see Fig. S10) in line with the results from the time dependent Ginzburg-Landau equation. We find that the sign of Q_2 , and thereby the magnetization, is determined by the sign of the coupling g .

We note that in addition to the ionic excitation mechanism, the Q_2 could in principle be excited via infrared-resonant Raman scattering (IRRS) or direct photon scattering. These mechanisms amount to replacing the $gQ_2Q_{\text{IR}}^2$ coupling term with either a $gQ_2Q_{\text{IR}}E(t)$ or $gQ_2E(t)^2$ coupling, respectively. To estimate the relative importance of the different excitation mechanisms, we extract the typical interaction energy of each mechanism, obtained by measuring g in meV, Q in terms of the oscillator length $l = 0.35a_0$ (with a_0 the Bohr radius), and E in units of 100 kVcm^{-1} . With these numbers, having calculated the Raman tensor from first principles, we find the photonic coupling to be of magnitude $g_{\text{phot}} = 0.5$ meV. For the IRRS coupling, we use a typical coupling $b \sim 1 \text{ e/V}$ [11], resulting in the interaction energy $g_{\text{IRRS}} = 0.04$ meV. Finally, for the non-linear phonon coupling, we use recent values from the isostructural compound MnPS₃ to find a typical coupling $g_{\text{phon}} = 1.3$ meV [12].

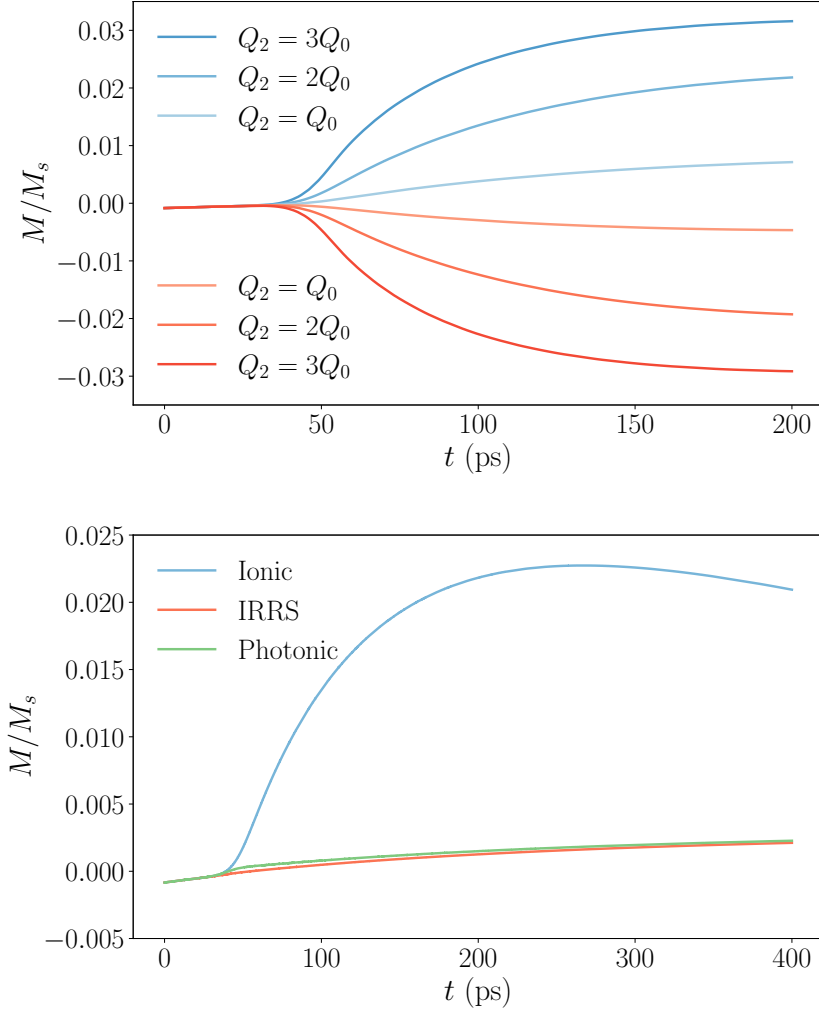


Fig. S 10. Dynamics of the THz-induced magnetization from atomistic spin dynamics simulations. (**Top panel**) Dynamics of the THz-induced magnetization M as a function of the magnitude and the sign of the 3.27 THz phonon displacement, Q_2 , resulting from atomistic spin dynamics simulations. The sign of the displacement is determined by the coupling constant g , as $Q_2 \sim gQ_{\text{IR}}^2$. (**Bottom panel**) Comparison of the magnitude of the ionic, infrared-resonant Raman scattering (IRRS) and photonic excitation mechanisms. The effective coupling strength g is kept fixed for all excitation mechanisms, while the coupling terms is taken to be $Q_2 \sim gQ_{\text{IR}}^2$ in the ionic case, $Q_2 \sim gQ_{\text{IR}}E(t)$ in the IRRS case, and $Q_2 \sim gE(t)^2$ in the photonic case, respectively.

Since these couplings are all of the same magnitude, we fix g in our numerical simulations. The contributions to the phonon displacement resulting from the different excitations are shown in Fig. 10, and show that the IRRS and photonic mechanisms are smaller than the ionic contribution by at least an order of magnitude.

10 Critical fluctuations and slowing down

To reconcile the above picture of a system with degenerate global minima at finite M and Q_2 , with the observations of a vanishing equilibrium magnetization and the long lifetime of the induced magnetization, we propose the following picture. We assume that the free energy landscape around the critical point is flat, such that the global minimum at $F(M_0)$ with $M = M_0$ is close in energy to the symmetric meta-stable solution at $F(0)$ with $M = 0$. More specifically, if the thermal energy $k_B T \approx F(0) - F(M_0)$, thermal fluctuations will allow the system to fluctuate between the two minima at $M = \pm M_0$, leading to a net average magnetization $\langle M \rangle = 0$. Similarly, thermal fluctuation of the phonon coordinate between the two solutions at $Q_2 = \pm Q_0$ will result in a zero average displacement $\langle Q_2 \rangle = 0$. This is similar to how fluctuations prevent ferroelectric ordering in SrTiO₃ [13], and a flat free energy landscape thus explains the equilibrium features of the system.

Now, once the system is kicked out of equilibrium by the THz pulse, the resulting net $\langle Q_2 \rangle$ will induce a finite magnetization $\langle M \rangle$ as discussed in the previous section. On short time scales compared to the characteristic relaxation time $\tau(T)$, this state will be stable. However, over long times $t \sim \tau(T)$ thermal fluctuations will once again build up and the system will return to its equilibrium state at $\langle M \rangle = 0$ and $\langle Q_2 \rangle = 0$. The net transient magnetization therefore follows from a laser-induced imbalance of the phonon coordinate (see Supplementary Note 9). In the following sections, we make this picture more precise.

Step 1: Adiabatic elimination of the phonon coordinate

To obtain the relaxation dynamics of the magnetization, we first show that an effective description of L and M can be obtained by replacing Q with its adiabatic value $Q(t) = -gL(t)M(t)/\Omega$. For this purpose we simulate the stochastic Ginzburg-Landau equations, as given by

$$\begin{aligned}\frac{\partial L}{\partial t} &= -\Gamma_L[a_L(T)L + b_L L^3 + gMQ] + \sqrt{2\Gamma_L k_B T} \xi_L(t) \\ \frac{\partial M}{\partial t} &= -\Gamma_M[a_M M + b_M M^3 + gLQ] + \sqrt{2\Gamma_M k_B T} \xi_M(t) \\ \frac{\partial Q}{\partial t} &= \frac{P}{m} \\ \frac{\partial P}{\partial t} &= -[\Omega Q + gLM] - \Gamma_Q P + \sqrt{2\Gamma_Q k_B T} \xi_P(t).\end{aligned}\tag{25}$$

Here the noise terms ξ_α are assumed to be Gaussian white noises, as defined by the correlations $\langle \xi_\alpha(t) \rangle = 0$ and $\langle \xi_\alpha(t) \xi_\alpha(t') \rangle = \delta(t - t')$. The long time limit of these equations can be shown to reproduce the probability distribution at thermal equilibrium, $P(L, M, Q) = e^{-\beta F}/Z$ with $Z = \text{Tr } e^{-\beta F}$.

By propagating the equations above, we study the relaxation from a given initial probability distribution $P_0(L, M, Q)$ towards the equilibrium distribution. This is done by sampling the initial distribution of the variables L , M and Q with a number of processes N , assuming the initial distribution is a Gaussian centered on the classical minimum (L_0, M_0, Q_0) and with variance σ . At given time t we then define the probability distribution $P_t(L, M, Q)$ as the normalized distribution of the instantaneous values of these N processes, i.e.

$$P_t(L, M, Q) = Z^{-1} \sum_i \delta(L_i(t) - L) \delta(M_i(t) - M) \delta(Q_i(t) - Q).\tag{26}$$

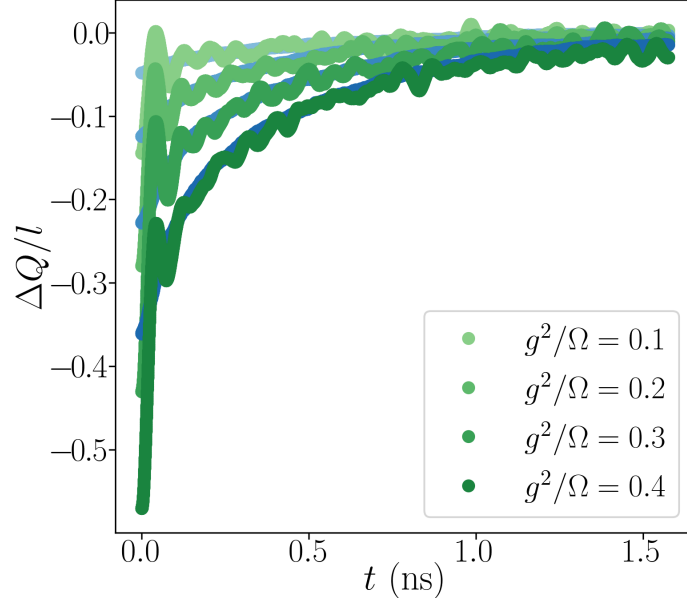


Fig. S 11. Adiabatic evolution of the phonon coordinate. Relaxation dynamics of the phonon coordinate (green) and the product $-gLM/\Omega$ (blue) as a function of coupling g , quantifying the increase in $L(0)^2$ close to T_N . Once the initial oscillations have been damped out, the phonon coordinate adiabatically follows the product $-gLM/\Omega$.

Here Z is a normalization constant. Given the instantaneous probability density, we study how the average antiferromagnetic order, net magnetization and phonon displacement return to their equilibrium values via the measures $\Delta L(t) = |L(t) - L_{\text{eq}}|$, $\Delta M(t) = |M(t) - M_{\text{eq}}|$ and $\Delta Q(t) = |Q(t) - Q_{\text{eq}}|$.

The relaxation dynamics is shown in Fig. S 11 as a function of the coupling strength g , which in equilibrium sets the depth of the double well potential for M via the effective parameter $\bar{a}_M = a_M - g^2 L^2 / \Omega$. As expected, the relaxation process is exponential at long times with a relaxation time increasing with the coupling. Importantly, we find that once the initial oscillations have been damped out, the phonon coordinate follows the product LM almost adiabatically (with the residual oscillations likely due to the finite number of sampling processes), such that the relaxation of M can be described by replacing $Q = -gLM/\Omega$ in the equations of motion.

Step 2: Critical slowing down of the dominant antiferromagnetic order parameter L

Next we demonstrate that the dominant antiferromagnetic order parameter L exhibits a critical slowing down as $T \rightarrow T_N$. From the theory of dynamical critical phenomena [9], it is known that the relaxation time of a critical system is related to its static susceptibility by $\tau = \chi/\Gamma$, where Γ is the kinetic coefficient appearing in the Ginzburg-Landau equation. The static magnetic susceptibility for L can be obtained from spin Monte Carlo simulations, and is shown in Fig. S12. As expected for a second order transition, it diverges as $T \rightarrow T_N$. Therefore, the relaxation time is also expected to undergo a critical divergence at T_N .

To further corroborate this finding, we solve the stochastic Ginzburg-Landau equations for L . Without

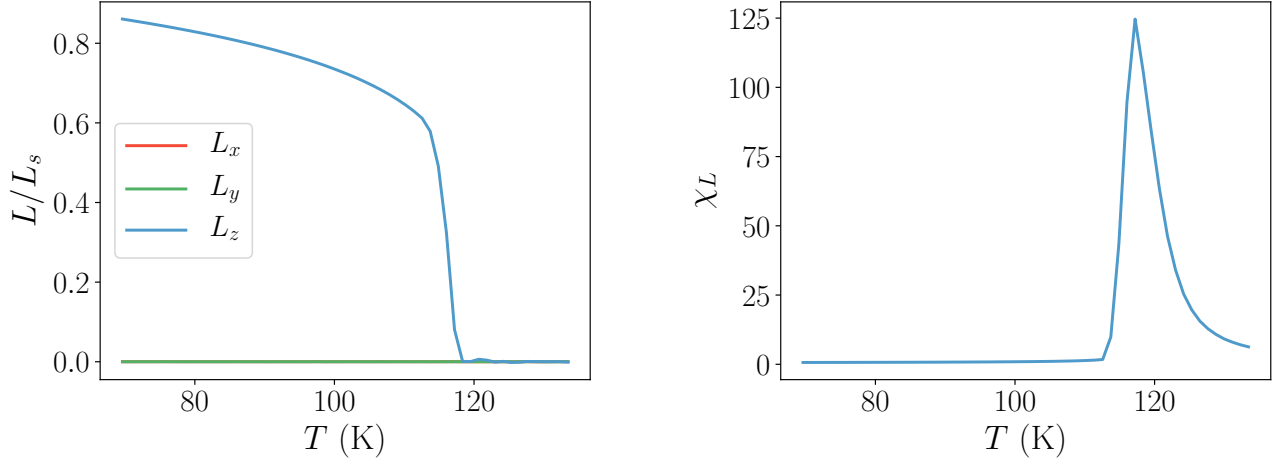


Fig. S 12. Critical properties of the antiferromagnetic order. Temperature dependence of the antiferromagnetic order parameter L and the corresponding susceptibility χ_L , obtained from spin Monte Carlo simulations of the microscopic spin model. Importantly, the susceptibility diverges as $T \rightarrow T_N$ (here the divergence is regularized by the finite size of the simulated system), signaling a critical slowing down of the order parameter dynamics.

the stochastic term, the equation for L can be solved analytically to obtain [14]:

$$L(t) = \frac{L(0)e^{-at}}{\sqrt{1 + \frac{b}{a}L(0)^2(1 - e^{-2at})}} \approx \frac{L(0)}{\sqrt{1 + \frac{2b}{a}L(0)^2t}} \sim \frac{1}{\sqrt{t}}, \quad (27)$$

demonstrating a polynomial decay instead of exponential decay for $T = T_N$. These results are consistent with the numerical solution of the stochastic equation, as shown in Fig. S13.

Although the above arguments qualitatively demonstrate the critical slowing down of the AFM order parameter dynamics, they are insufficient to quantitatively capture the correct functional form and dynamical exponents of the relaxation process. For this reason, we assume in the following that the antiferromagnetic order parameter decays as $L(t) = L(0)e^{-t/\tau}$ with $\tau \sim |T - T_N|^{-\nu_z}$, as found in renormalization group calculations [9].

Step 3: Critical slowing down of the magnetization M

The relaxation dynamics of the magnetization M follows from the stochastic Ginzburg-Landau equation for M , where we assume an exponential decay of $L(t)$ in agreement with the renormalization group calculations. This is achieved by neglecting the effects of M on the critical properties of L , an assumption which is validated by our spin Monte Carlo simulations (see Fig. S4). In addition to the divergence of τ as $T \rightarrow T_N$, also $L(0)$ is expected to increase close to the Néel temperature, as the flat free energy landscape makes L more sensitive to the phonon displacement. To quantify this effect, we define the effective coupling parameter $\lambda^2 = g^2L(0)^2/\Omega$ and study the relaxation of M as a function of λ .

The resulting equations to solve are then:

$$\frac{\partial L}{\partial t} = -\Gamma_L L + \sqrt{2\Gamma_L k_B T} \xi_L(t)$$

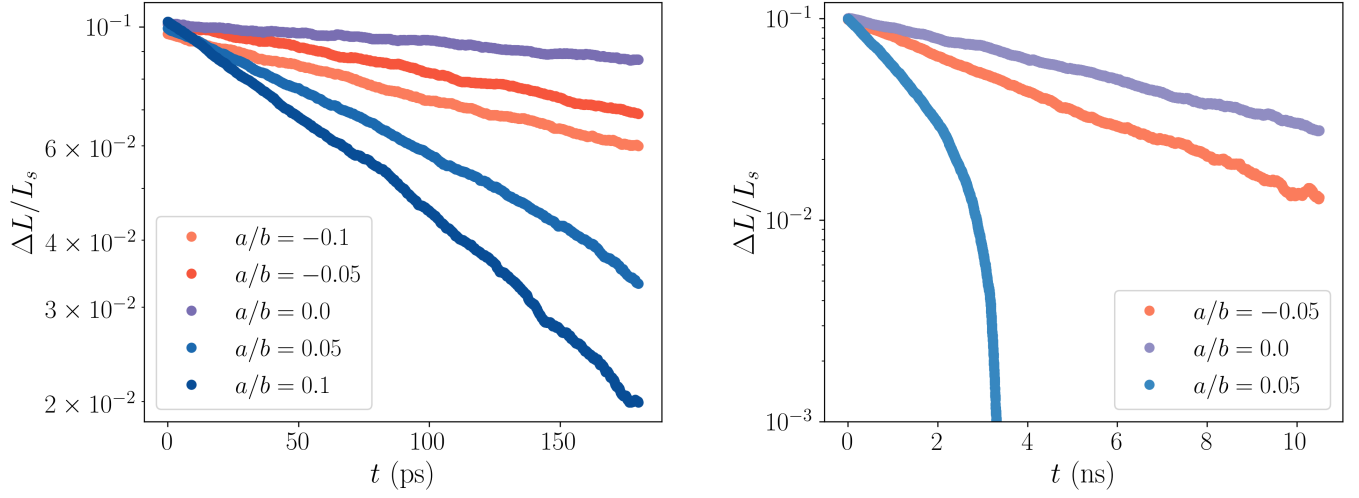


Fig. S 13. Critical slowing down of the antiferromagnetic order. Relaxation of the antiferromagnetic order parameter for different values of the quadratic parameter a of the Ginzburg-Landau free energy (with the quartic coefficient fixed at $b = 10$ meV). Critical slowing down is observed when $a \rightarrow 0$ (purple line), as expected when $T \rightarrow T_N$. In the left panel we use $\Gamma_L = 1$ meV, while in the right panel we use $\Gamma_L = 0.1$ meV

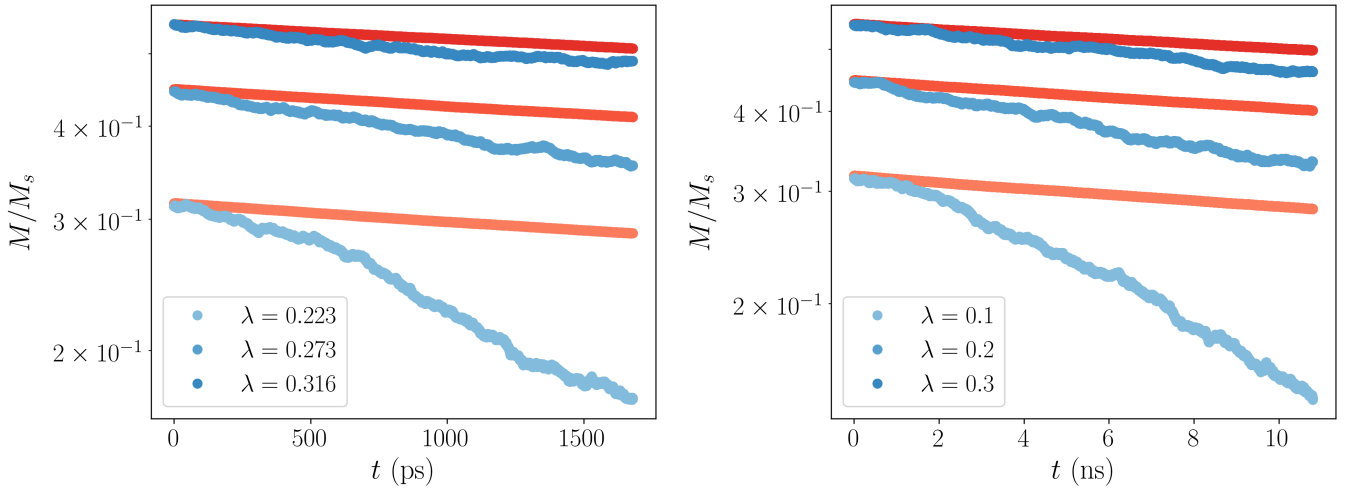


Fig. S 14. Critical slowing down of the magnetization dynamics. Relaxation dynamics of the magnetization (blue) and antiferromagnetic order (red) as a function of coupling $\lambda = g^2 L(0)^2 / \Omega$ (given in meV). As we approach the critical point, the relaxation of M approaches that of L . The parameters are $a_L = 0$, $b_L = 5$ meV, $a_M = 1$ meV, $b_M = 10$ meV and $\Omega = 5$ meV. In the left panel we use $\Gamma_L = \tau^{-1} = 10^{-2}$ meV and $\Gamma_M = 1$ meV, while in the right panel we use $\Gamma_L = \tau^{-1} = 2 \times 10^{-3}$ meV and $\Gamma_M = 0.2$ meV.

$$\frac{\partial M}{\partial t} = -\Gamma_M \left(a_M M + b_M M^3 - \lambda^2 \frac{L(t)^2}{L(0)^2} M \right) + \sqrt{2\Gamma_M k_B T} \xi_M(t), \quad (28)$$

where $\Gamma_L = \tau^{-1}$. The resulting dynamics are displayed in Fig. S14, and we note that with increasing τ and λ , the dynamics of M approaches the dynamics of L . In the limit $T \rightarrow T_N$ the dynamics of M thereby inherits the critical slowing down from L , such that close to T_N we have $M(t) \sim e^{-t/\tau}$.

An intuitive way to understand this result is to note that for $T \rightarrow T_N$, the fast order parameter M quickly decays to the local minimum defined by the slow order parameter L . Once M has reached this minimum, it adiabatically follows it back to equilibrium, such that $M(t) \approx \sqrt{(g^2 L(t)^2 / \Omega - a_M) / b_M}$. More precisely, we note that for slow variations of L (i.e., close to criticality), we can approximately solve the deterministic Ginzburg-Landau equation for M by replacing a_M with $\bar{a}_M = a_M - g^2 L(t)^2 / \Omega$. The solution is then (cf. Eq. 27 above)

$$\begin{aligned} M(t) &\approx \frac{M(0)e^{-at+\lambda^2\tau e^{-t/\tau}}}{\sqrt{1 + \frac{b}{a+\lambda^2 e^{-t/\tau}} M(0)^2(1 - e^{-2at+2\lambda^2\tau e^{-t/\tau}})}} \\ &= \sqrt{\frac{\lambda^2 e^{-t/\tau} - a}{b}} \frac{1}{\sqrt{1 - e^{2at-2\lambda^2\tau e^{-t/\tau}}(1 + \frac{a+\lambda^2 e^{-t/\tau}}{b} M(0)^{-2})}}, \end{aligned} \quad (29)$$

where we have suppressed the subscripts on a_M and b_M . The leading order term of this equation recovers the simple adiabatic approximation discussed above, while the sub-leading terms show that there is a crossover at $at \approx \lambda^2 \tau e^{-t/\tau}$ to a regime of intrinsic exponential decay $M(t) \sim e^{-at}$. Importantly, close to the critical temperature, $M(t)$ will decay with a diverging relaxation time $\tau \sim |T - T_N|^{-\nu z}$.

Summary

As demonstrated by the sections above, close to the critical temperature the relaxation time of the magnetization M is set by the relaxation time of the antiferromagnetic order parameter L . Being the dominant order parameter at a second order phase transition, L in turn shows a critical slowing down of the form $L(t) \sim e^{-t/\tau(T)}$, where $\tau(T) = \tau_0 [T_N / (T - T_N)]^{\nu z}$. Therefore, also the magnetization will decay on a time scale set by $\delta M(t) \sim e^{-t/\tau(T)}$, leading to the extremely long lifetime observed in our experiments. For the 3-D (2-D) Ising model, the dynamical exponents are $\nu = 0.62997$ ($\nu = 1$) and $z \approx 2.02$ ($z = 2.14$), giving a relaxation time that scales as

$$\tau(T) = \tau_0 \left(\frac{T_N}{T - T_N} \right)^{\nu z} \quad (30)$$

with $\nu z \approx 1.27$ ($\nu z \approx 2.14$).

11 Measurement schemes for the polarization state of light

The polarization of light field propagating along the z -direction is described by the Jones vector:

$$\mathbf{E} = \begin{pmatrix} E_{0x} \\ E_{0y} e^{i\delta} \end{pmatrix}. \quad (31)$$

where E_{0x} and E_{0y} are the amplitude of the electric field along x and y directions, and δ is their phase difference. We define $\tan \alpha = \frac{E_{0y}}{E_{0x}}$ to characterize the ratio between y and x electric field amplitudes. In general, Eq. 31 describes an elliptically polarized light. An ellipse is defined by the polarization angle ψ (the angle between the major axis of the ellipse and the x axis) and ellipticity angle χ (the ratio between the minor and major axis), which are related to α and δ by [15]:

$$\tan(2\psi) = \tan(2\alpha) \cos \delta \quad (32)$$

$$\sin(2\chi) = \sin(2\alpha) \sin \delta, \quad (33)$$

In our experiments, to measure the static dielectric properties of FePS₃, a vertically polarized light impinges on the sample and the polarization of the transmitted light is measured by balanced detection schemes. In the first scheme, the transmitted light passes through a half-wave plate (HWP) with its fast axis aligned along 22.5° with the y axis. We then separate the x and y components of the light with a Wollaston prism and measure their intensities I_x and I_y . We define the balanced detection signal as

$$\frac{\Delta I}{I} = \frac{I_y - I_x}{I_y + I_x}. \quad (34)$$

$\frac{\Delta I}{I}$ can be related to elliptical polarization parameters (ψ, χ) of the light transmitted through the sample as derived in the following. The polarization state of the light after the HWP is given by

$$R\left(-\frac{\pi}{8}\right) \begin{pmatrix} 1 & 0 \\ 0 & e^{i\pi} \end{pmatrix} R\left(\frac{\pi}{8}\right) \mathbf{E} = \begin{pmatrix} \frac{\sqrt{2}E_{0x}}{2} + \frac{\sqrt{2}E_{0y}e^{i\delta}}{2} \\ \frac{\sqrt{2}E_{0x}}{2} - \frac{\sqrt{2}E_{0y}e^{i\delta}}{2} \end{pmatrix}, \quad (35)$$

where R is the two-dimensional rotation matrix and the 2×2 matrix in the middle is a Jones matrix for HWP. The balanced detection signal is then given by

$$\left(\frac{\Delta I}{I}\right)_{\text{HWP}} = -\frac{2E_{0x}E_{0y}\cos\delta}{E_{0x}^2 + E_{0y}^2} = -\tan(2\psi)\cos(2\alpha). \quad (36)$$

In the second scheme, we replace the HWP by a quarter-wave plate (QWP) with its fast axis aligned 45° with y axis. Now the polarization state after the QWP is

$$R\left(-\frac{\pi}{4}\right) \begin{pmatrix} 1 & 0 \\ 0 & e^{i\frac{\pi}{2}} \end{pmatrix} R\left(\frac{\pi}{4}\right) \mathbf{E} = \begin{pmatrix} \frac{(1-i)(iE_{0x}+E_{0y}e^{i\delta})}{2} \\ \frac{(1-i)(E_{0x}+iE_{0y}e^{i\delta})}{2} \end{pmatrix}, \quad (37)$$

here the 2×2 matrix in the middle is a Jones matrix for QWP. And the balanced detection signal in this case is:

$$\left(\frac{\Delta I}{I}\right)_{\text{QWP}} = -\frac{2E_{0x}E_{0y}\sin\delta}{E_{0x}^2 + E_{0y}^2} = -\sin(2\chi) \quad (38)$$

In the limit of small sample modulation of optical properties $\alpha - \frac{\pi}{2} \ll 1$, $\delta \ll 1$, we have

$$\left(\frac{\Delta I}{I}\right)_{\text{HWP}} \approx 2\psi - \pi \quad (39)$$

$$\left(\frac{\Delta I}{I}\right)_{\text{QWP}} \approx -2\chi. \quad (40)$$

Therefore we can directly probe the polarization angle, ψ and the ellipticity angle, χ , of the light transmitted through the sample by using HWP and QWP, respectively, in the balanced detection scheme. The results are shown in Fig. 1b and c of the Main Text.

12 Relating the ellipticity and polarization angle to the complex refractive index

To relate the ellipticity χ and polarization ψ angles to the optical properties of a solid we consider the complex transmission coefficient through a slab of material with complex refractive index $\tilde{n} = n + ik$,

$$T = \tau_1 \tau_2 \exp(-ik_0 n \cdot l) \quad (41)$$

where $\tau_i = 1 + \rho_i$ are the elementary transmission coefficients and $\rho_i = \pm \frac{n-1}{n+1}$ are the elementary transmission coefficients of front and back interfaces, respectively. l is the slab thickness and k_0 is the wavenumber of the transmitted light in vacuum. As outlined above, in the limit of small δ we have $\psi \approx \alpha$ and the polarization angle ψ is then determined by the two electric field components as $\tan \psi_0 = \frac{E_{0y}}{E_{0x}}$ and therefore the polarization angle of the transmitted light is determined by the ratio of the absolute values of $\frac{|T_y|}{|T_x|}$, and is given by:

$$\tan \psi = \tan \psi_0 \times \frac{|\tau_{1,y}| |\tau_{2,y}| \exp(-k_0 k_y \cdot l)}{|\tau_{1,x}| |\tau_{2,x}| \exp(-k_0 k_x \cdot l)} \quad (42)$$

$$= \tan \psi_0 \times \sqrt{\frac{n_y^2 + k_y^2}{n_x^2 + k_x^2}} \times \frac{(n_x + 1)^2 + k_x^2}{(n_y + 1)^2 + k_y^2} \times \exp(-k_0(k_y - k_x) \cdot l) \quad (43)$$

$$\approx \tan \psi_0 \times \exp(-k_0(k_y - k_x) \cdot l) \quad (44)$$

The last step involves make use of $\tilde{n}_y \approx \tilde{n}_x$, which is typically a good approximation even for dichroic or birefringent materials. Moreover, in this limit the prefactor of the exponential $\sqrt{\frac{n_y^2 + k_y^2}{n_x^2 + k_x^2}} \times \frac{(n_x + 1)^2 + k_x^2}{(n_y + 1)^2 + k_y^2}$ will be close to 1 for the experimental values of $n \approx 3$ and $k \approx 0.1$ [16]. The factor in the exponential $k_0 \cdot l$ is in the order to 1000 for the thickness of the sample ($\sim 200 \mu\text{m}$) and probe wavelength (800 nm). *Therefore, the polarization angle $\Delta\psi = \psi - \psi_0$ is determined by the imaginary part of the refractive index in a material with a linear dichroism $k_y \neq k_x$.* Similar arguments can be made for the ellipticity angle χ . From the above discussion we know, that χ is proportional to the retardation difference δ of the two orthogonal electric field components. After propagating through the material slab the retardation difference is given by the difference of the argument of the complex transmission coefficient along x and y ,

$$\Delta\delta = \arg(T_y) - \arg(T_x) = \arg\left(\frac{T_y}{T_x}\right) \quad (45)$$

This can be derived as,

$$\Delta\delta = k_0(n_y - n_x) \cdot l + \arg\left(\frac{n_y + ik_y}{n_x + ik_x} \cdot \frac{(n_x + 1 + ik_x)^2}{(n_y + 1 + ik_y)^2}\right) \quad (46)$$

with the same argument as above ($n_y \approx n_x$ and $k_0 \cdot l$ is large), this can be approximated as:

$$\Delta\delta = k_0(n_y - n_x) \cdot l \quad (47)$$

This result shows that ellipticity angle χ is determined by the real part of the refractive index in a material with a linear birefringence $n_y \neq n_x$.

13 The insensitivity of the sign of THz-induced magnetization to domain formation

In a bulk sample, the system consists of a magnetic unit cell containing a total of 8 Fe ions, accounting for the zigzag antiferromagnetic order within each layer as well as the antiferromagnetic interlayer coupling. A change in sign of all spins, corresponding to a change in sign of L , is therefore equivalent to a translation of the system along the interlayer direction c by a distance $c/2$. Since the choice of unit cell should not affect any physical properties, this means that we also need to change the sign in the definition of the phonon displacement Q_2 . This follows from the fact that Q_2 is a Raman mode and has to be even under inversion symmetry. For the magnetization order parameter, no change in sign is necessary between the unit cells. Therefore, reversing the sign of L should be associated with a simultaneous change of sign in Q_2 , ensuring that the coupling term $gLMQ_2$ remains invariant. This property indeed has important consequences for the stability of the observed effect, implying that it is insensitive to domain formation.

To illustrate this insensitivity to the domain structures more closely, we consider two domains with $L > 0$ and $L < 0$ (Fig. S15). As explained earlier, the lattice distortions in the neighboring layers have to be in opposite directions due to Raman activity of the mode. For instance, in the upper layer (Layer 1) of Domain 1 (Fig. S15a), the zig-zag chains with up spins (shown in red) acquire stronger magnetic exchange interactions under the distortion, whereas the chains with down spins acquire weaker magnetic interactions. This results in a net positive (up) magnetization. Meanwhile, in the lower layer (Layer 2), the distortion occurs in the opposite direction, again leading to positive magnetization. All these magnetizations add up. A domain with opposite sign of antiferromagnetic (AFM) order parameter (Domain 2), has to be distorted with the opposite Q_2 (Fig. S15b), also leading to positive (up) magnetization ($M > 0$).

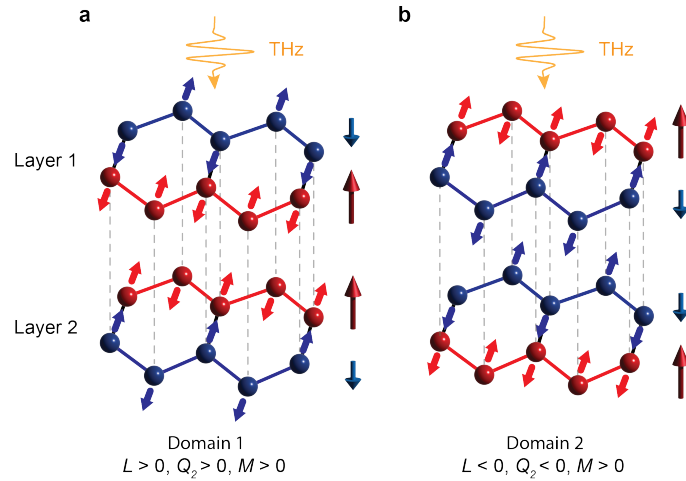


Fig. S 15. The sign of THz-induced magnetization **a.** A lattice distortion of Domain 1 with $L > 0$, under the nonlinear excitation of the Q_2 phonon. Two neighboring layers are depicted. Under such distortion, upper and lower layers have opposite phase of the distortion, leading to $M > 0$ in each layer. **b.** same for Domain 2, with $L < 0$ and correspondingly $Q_2 < 0$.

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